AGING OF REGENERATED FILM-FORMING SOLUTIONS

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The kinetics of time-varying physical properties of film-forming solutions and films is considered. The dependences existing between the state of the disperse phase of a sol, its light transmission, refractive index, and the physical properties and structure of the coatings are established. The regularities of the aging of solutions and the effect of various factors on this process are described.

In [1] we discussed the results of the study of the process of aging of film-forming solutions (FFS) in which ethanol extracted from worked-out sols acted as a solvent, as well as the kinetics of variation of the physical properties and microstructure of the respective sol-gel coatings. The objets of experiment, experimental procedures, and methods for isolating the secondary alcohol described in detail in [1] are used in the present study.

Table 1 shows certain properties of solutions and coatings, as well as the batch numbers of secondary ethanol differing in their qualitative and quantitative compositions due to the specifics of ethanol extraction (the respective FFS and coatings have the same numbers).

Divide all film-forming solutions into four categories based on the light transmission parameter. Each sol is coded with a group of digits and letters. For example, $1B_{22}(O)$ means that the given sol is prepared from 1B alcohol, the age of the FFS is 22 days, and a precipitate consisting of film-forming oxides and(or) salts can be visually observed in it. The letter "T" in brackets points to the turbidity of the given solution. If a FFS is transparent and has no precipitate, there are no letters in brackets.

Light transmission of FFS, %	Solution groups in the same category by the light transmission parameter
50,0 – 60,0	O_2, $2A_{42}(O, T)$
60,1 – 70,0	$1A_2$, $1B_2$, $1B_8(T)$, $1B_{15}(O,T)$, $2A_2$, $2A_{15}(O, T)$, $2A_{22}(O, T)$, $2B_2$, $2B_8(T)$, $2B_{22}(O, T)$
70,1 – 80,0	O_8, O_{15}, O_{22}, O_{42}, $1A_{22}$, $1B_{22}(O)$, $2A_8$, $2B_{15}$
80,1 – 90,0	$1A_8$, $1A_{15}$, $1A_{42}$, $1B_{42}(O)$, $2B_{42}(O)$

Figure 1 represents the photos of all coatings. Since the microstructure of a coating significantly depends on the state of the disperse phase of sol [2], let us discuss the available data.

It can be seen that the lowest level of light transmission is exhibited by two FFS (or 8% of the total number of sols investigated). The intense light losses in the visually transparent O_2 solution are probably related to radiation diffusion through numerous unilaterally oriented chain (flagellum-shaped) particles with a cross section up to 0.3 µm and a length comparable with the coated glass thickness. Similar phenomena are probably the reason for low light transmission of the $2A_{42}$ solution which is turbid and contains a precipitate. Its disperse phase is represented by numerous grains whose maximum diameter is 0.2 µm.

The next group of solutions with a higher level of light transmission includes 10 sols (or 40% of the total number), among them four visually transparent and six turbid. The four turbid FFS formed a precipitate. The light transmission of the transparent solutions and the turbid solutions with a precipitate is slightly higher than that of the turbid solutions without precipitate. Apparently, the turbid solutions contain a high amount of large particles. Indeed (Fig. 1), the number of inclusions in the respective films is an order of magnitude higher than in the coatings obtained from transparent solutions. At the same time, the length of some chains reaches 3 µm and more, and the diameter of spheroid particles reaches 0.8 – 1 µm. It is known [3] that the greater the size of the particles, the higher are its chances for sedimentation; therefore, it is logical to expect that the light transmission of turbid solutions with a precipitate will be higher due to a decrease in the amount and size of the light-diffusing disperse phase. This is supported by the data in Table 1 and the photos in Fig. 1

The light transmission of the next eight solutions (which is 32% of the total investigated solutions) is within the limits of 70.1 – 80%. All of them are transparent, and only one of them ($1B_{22}$) contains a sediment. The microstructure of the respective films is more homogeneous than in the preceding group of films: the chain inclusions are shorter and thinner.

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However, coarse inclusions up to 0.1 μm are found in two films (O_{22} and $2A_8$). This fact accounts for the light transmission values of the respective FFS which are the lowest for this group: 71.2 and 72.6%, respectively. After the formation of a sediment, the light transmission of the transparent sol $1B_{22}$ regularly increases up to 77.4%, although the microstructure of the film is relatively coarse.

The light transmission of the last five solutions (or 20% of all studied solutions) varies from 80.1 to 90.0%. All of them are visually transparent. In two of them ($1B_{42}$ and $2B_{42}$) a sediment is present, and these solutions have the maximum light transmission, although the microstructure of the respective films is highly coarse (Fig. 1) The light transmission of the three solutions without precipitate is slightly lower (80.2 – 81.8%) due to the increase, by an order of magnitude, of the number of disperse particles compared to the solutions with precipitates.

In general, the minimum light transmission was observed in the turbid (less often in the visually transparent) sols with

a large part by volume of the disperse phase, regardless of the shape of the particles. The maximum light transmission was found in transparent solutions with a sediment, and their disperse phase was represented by scarce and rather coarse particles.

The refractive index of the solutions markedly depends on the existence of an excess of highly refractive components (HCl and NH_4Cl) whose presence is caused either by specific features of extraction of secondary ethanol, or by the technology of FFS preparation [1]. Therefore, the refractive index of 14 solutions of the 1A, 1B, and 2B ($2A_{2-42}$, $1B_{2-42}$, $2B_{8-42}$) series is slightly higher than that of the remaining ten solutions (O_{2-42}, $1A_{2-42}$). An exception is $2B_2$ solution whose refractive index is abnormally low compared to other sols of the 2B series.

Table 1 shows an inversely proportional dependence between the light transmission and the refractive index of the FFS. Indeed, the refractive index of a particular medium is determined by the velocity of light propagation in this me-

TABLE 1

| Series	Properties of FFS			State of FFS		Confidence intervals for the distribution of values	
	age, days	refractive index	light transmission coefficient, %	presence of sediment	presence of turbidity	refractive index	mirror reflection coefficient, %
1A	2	1.388	64.6	–	–	2.14 – 2.09	41.0 – 38.4
	8	1.387	80.2	–	–	2.16 – 2.12	41.7 – 38.1
	15	1.387	81.8	–	–	2.06 – 2.02	30.9 – 30.3
	22	1.387	77.6	–	–	2.08 – 1.97	30.7 – 25.8
	42	1.383	80.5	–	–	1.82 – 1.77	20.7 – 20.3
1B	2	1.393	62.3	–	–	1.92 – 1.74	30.5 – 29.9
	8	1.393	60.4	–	+	1.81 – 1.74	33.0 – 20.4
	15	1.392	67.1	+	+	1.98 – 1.84	25.3 – 23.9
	22	1.392	77.4	+	–	1.82 – 1.80	18.8 – 18.2
	42	1.391	84.0	+	–	1.81 – 1.68	17.5 – 16.9
2A	2	1.394	64.8	–	–	2.01 – 1.93	22.2 – 21.6
	8	1.393	72.6	–	–	2.08 – 1.89	28.7 – 27.7
	15	1.392	64.1	+	+	1.74 – 1.65	11.8 – 11.6
	22	1.391	62.3	+	+	1.71 – 1.61	16.9 – 16.5
	42	1.391	58.8	+	+	1.73 – 1.64	13.7 – 13.1
2B	2	1.383	68.5	–	–	1.97 – 1.88	25.0 – 24.9
	8	1.392	62.9	–	+	1.98 – 1.84	26.6 – 27.2
	15	1.392	75.7	+	–	2.02 – 1.80	22.5 – 19.9
	22	1.392	65.1	+	+	2.00 – 1.75	17.0 – 16.8
	42	1.390	85.6	+	–	1.61 – 1.54	15.3 – 14.7
O	2	1.389	57.3	–	–	2.23 – 2.21	40.0 – 38.8
	8	1.388	76.9	–	–	2.19 – 2.15	39.6 – 38.0
	15	1.387	77.3	–	–	2.20 – 2.17	42.7 – 42.5
	22	1.388	71.2	–	–	2.08 – 1.96	30.6 – 30.4
	42	1.387	77.1	–	–	1.83 – 1.73	22.8 – 21.2
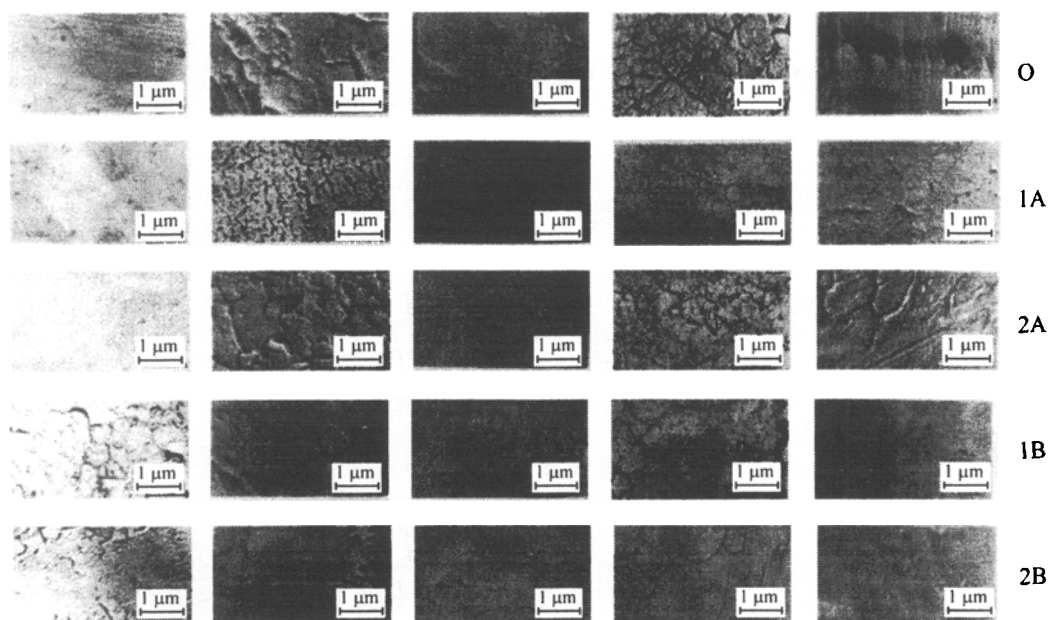
Fig. 1. Electron microscopic photos of the films obtained from solutions of different ages (UEMV-100 K electron microscope, ×10,000).

dium [4]. The latter is related to the presence and quantity of the diffusing phase.

The turbidity of the sols is attributed to the increase in the size of colloidal particles due to agglomeration of smaller particles. It produces a decrease in the amount of particles and the part by volume of the disperse phase in a FFS. That is why the refractive index of turbid solutions $1B_8$ and $2B_8$ is higher than that of the "younger" transparent solutions $1B_2$ and $2B_2$.

After the formation of a precipitate, the refractive index of a FFS either does not change ($1B_{15}$, $1B_{22}$, $2B_{15}$, $2B_{22}$) or decreases insignificantly ($1B_{42}$, $2A_{15}$, $2A_{22}$, $2B_{42}$).

Many low-boiling and(or) easily decomposed components (the boiling point is 100°C for water, 78.4°C for ethanol, and 340°C for hydrogen chloride [5]), which determine the refractive index of the FFS, are completely or partially removed after film deposition, its drying, and firing at a temperature of 450°C. This depends on the concentration of the specified components, the degree of their coherence to the film-forming oxides and the strength of the emerging compounds. Therefore, it can be assumed that no proportional dependence will exist between the refractive index of the solutions and the refractive index of the films. Indeed, two sols ($1A_{42}$ and $2B_2$) have an identical refractive index equal to 1.382. However, the confidence intervals of the distribution of the refractive index values in the coatings obtained from these FFS are not equal (they are 1.82 – 1.77 and 1.97 – 1.88, respectively). A similar situation in observed in six coatings obtained from solutions $1B_{15}$, $1B_{22}$, $2A_{15}$, $2B_8$, $2B_{15}$, $2B_{22}$, which all have the same refractive index of 1.392. The confidence intervals of the distribution of the minimum and maxi-

mum refractive index values of these films vary from 2.0 – 1.8 to 1.74 – 1.65.

Apparently, there ought to be a dependence between the light transmission of a FFS and the mirror reflection coefficient of the film, sine the shape, size, and quantity of inclusions in a coating are closely related to the state of the disperse phase of the sol [2]. The former will determine the mirror reflection coefficient of the coating, and the latter will determine the light transmission of the solution. It is known that there is a linear dependence between the refractive index and the mirror reflection coefficient of a thin film [6]. Experience has shown that the real coatings often exhibit a deviation from the above-mentioned regularity.

Let us consider the investigated films. The coatings O_2, O_8, and O_{15} have very similar refractive indexes and logically their mirror reflection indexes should be equal. In fact (Table 1), the maximum mirror reflection coefficient is exhibited by the film O_{15} obtained from a transparent sol with the highest light transmission level of 77.3%. Similar regularities can also be observed in the FFS and coatings made of composition $2A_2$ and $2A_8$. With occurrence of a sediment or turbidity in a solution, this dependence is disturbed. The reason consists in significant gradation of disperse particles by size in the turbid FFS, which probably persists in the raw film. After firing, the fine particles of the film have more chances of being completely melted and assimilated by the coating matrix, and the coarse particles persist and form a light-diffusing phase, which decreases the mirror reflection coefficient of the film. Therefore, a correlation of several films obtained from the turbid film-forming solutions, such as $1B_8$, $1B_{15}$, and $1B_{42}$, with similar refractive indexes (Table 1) established that the highest mirror reflection coeffi-

cient is exhibited by $1B_8$ coating corresponding to the sol with the minimum light transmission level of 60.4%. The part by volume of the light-absorbing and(or) diffusing disperse phase in this sol is sufficiently high and is probably represented among others by the fine particles easily melted in heat treatment of the coating. A similar dependence is also observed in $2B_8$, $2B_{15}$, and $2B_{22}$ solutions and films.

In each of the five investigated series the refractive index of sols decreases with aging (the only exception is the $2B_2$ solution with an abnormally low refractive index).

In the aging of deposited FFS, the refractive index and the mirror reflection coefficient of the coatings decrease, which is supported by the data in [1]. After the appearance of precipitates consisting mainly of titanium dioxide [2], 1B, 2A and 2B sols are depleted in a high-refractive polymer-forming component (note that the solution for film deposition in the experiment was taken from above the precipitate, since it was found that the precipitate grains penetrating into a film after intense agitation sharply deteriorate the quality of the coating). This brings about a decrease in the refractive index, and the mirror reflection coefficient decreases even more due to deterioration of the solution spreadability on glass and the emergence of light-diffusing fissures in the film.

It is known that water and a catalyst of titanium alkoxide hydrolysis (in our case, it is hydrochloric acid) accelerate the ripening of sol [6]. The investigated FFS are no exceptions. Both solutions of the B series prepared from secondary ethanol enriched with water become turbid on the 8th day, and the 15-day sols exhibit a clearly perceptible dense sediment. The negative effect of hydrochloric acid is less perceptible: the 2A sol, which was prepared with an excess of hydrochloric acid, retains its transparency on the 8th day but on the 15th day the solution becomes turbid, and formation of a sediment begins in it. Only two FFS (O_{2-42} and $1A_{2-42}$) retain complete transparency without traces of sedimentation over the entire 42-day experimental cycle, which is probably related to their balanced content of water and acid.

In order to assess the efficiency of specific methods for regeneration of alcohol and recommend the optimum one, let us contrast the kinetics of time-varying physical properties of the FFS and solutions (Table 1) and the transformation of the

coating microstructure (Fig. 1) of the reference series O (in which industrially manufactured hydrolysis alcohol acted as a solvent) with the same parameters of the sols and films of the remaining series. The 1 A solution and coating have properties which are the nearest to the reference properties. It agrees with the conclusion in [1] suggesting that the method of alcohol isolation from worked-out FFS is the optimal one. Recall that it involves precipitation of FFS with caustic alkali, isolation of the precipitate, and distillation of the filtrate at a temperature of 78 – 80°C.

Thus, the light transmission of sols depends on the state of the disperse phase. The maximum light transmission is seen in transparent solutions with a sediment and few coarsely disperse colloidal particles, and the minimum light transmission is exhibited by turbid (occasionally by transparent) solutions with a large fraction of the disperse phase. The refractive index of turbid solutions is higher than that of transparent ones. The refractive index of the films does not depend on the refractive index of the solutions. In some cases, a linear dependence between the light transmission of sols and the mirror reflection coefficient of the respective films was registered. This regularity is disturbed with the appearance of sediments in the FFS. The kinetics of solution aging and the rate of emergence of precipitate are closely related to the content of water and acid in the FFS, the water having a stronger effect.

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